

## 华南五种木兰科植物精油成分和抗氧化活性<sup>\*</sup>

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**摘要:** 对广东南岭自然保护区内野生的毛桃木莲 (*Manglietia moto*)、乳源木莲 (*M. yuyanensis*)、乐昌含笑 (*M. chapensis*)、金叶含笑 (*M. foveolata*) 和深山含笑 (*M. maudiae*) 5 种木兰科芳香植物精油进行了化学成分对比分析和抗氧化活性研究。化学成分鉴定采用气质联用技术, 同时结合了保留指数比较法; 精油抗氧化活性采用  $\beta$ -胡萝卜素漂白试验法。深山含笑芳香精油的主体成分以单萜烯为主, 另外 4 种木兰科芳香精油所含成分均以倍半萜类为主。毛桃木莲和乳源木莲精油在成分构成上具有高度一致性, 而且在主要成分上具有相似性, 这可能表明它们具有非常近的植物亲缘关系。4 种精油的抗脂质氧化半抑制浓度分别为 6.6 g/L (毛桃木莲精油)、9.8 g/L (乳源木莲精油)、11.3 g/L (金叶含笑精油) 和 12.2 g/L (乐昌含笑精油), 在本试验条件下, 未能测出深山含笑的半抑制浓度。

**关键词:** 木兰科; 芳香植物; 精油; 气质联用成分分析; 抗氧化活性;  $\beta$ -胡萝卜素漂白法

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## Chemical Composition and Antioxidant Activities of the Essential Oils of Five Magnoliaceae Species from South China

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**Abstract:** The essential oils of five Magnoliaceae plants, namely *Manglietia moto* Dandy, *Manglietia yuyanensis* Law, *Michelia chapensis* Dandy, *Michelia foveolata* Merr. ex Dandy, and *Michelia maudiae* Dunn, growing wild in Nanling National Nature Reserve of Guangdong province, were analyzed for their chemical composition and tested for their antioxidant effectiveness. The GC-MS analyses as well as comparison of the retention indices (RI) of elution peaks with literature data were used in compound identification of the essential oils; the  $\beta$ -carotene bleaching (BCB) test method was used in the preliminary evaluation of antioxidant activities for them. The *M. maudiae* oil characterizes high contents of monoterpenes, while other four oils are all constituted mainly by sesquiterpenoids. The high consistence of composition and similarities in major constituents between the *M. moto* and *M. yuyanensis* oils may indicate their close correlation between relatives. The 50% inhibition were accomplished with 6.6 g/L of *M. moto* oil, 9.8 g/L of *M. yuyanensis* oil, 11.3 g/L of *M. foveolata* oil and 12.2 g/L of *M. chapensis* oil, respectively, whereas *M. maudiae* oil could not inhibit 50% of the bleaching reaction under the test conditions.

**Key words:** Magnoliaceae; Aromatic plant; Essential oils; GC-MS analysis; Antioxidant activity;  $\beta$ -carotene bleaching

The family Magnoliaceae belonging to the most 260 species (Law, 1984). China occupies maximum ancient angiosperm, comprises about 15 genera and numbers of genus and species of Magnoliaceae in the

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world (11 genera and 150 species, respectively) (Xu *et al*, 2000). Many species are famous ornamentals because of their beautiful flowers and tree forms, and some species have been well known as important components of some Chinese traditional medicines for the treatment of gastrointestinal disorders and anxiety for more than 2000 years (Liu, 2003; Li, 2002; Zhu *et al*, 1997; Tachikawa *et al*, 2000).

*Michelia* and *Manglietia* are two big genera of Magnoliaceae and both are endemic in Asia (58 and 33 species in China, respectively). These species are mainly used as garden plants while some of them are also used in folk medicine to treat sore, fever, rhinitis, bronchitis, prostatitis, leucorrhea and pharyngitis (Shang *et al*, 2002; Bi *et al*, 2004). Analysis of volatile constituents from several above species has revealed the presence of monoterpenes, sesquiterpenes and their derivatives that have shown interesting antioxidative, antimicrobial, and vasodilator activities (Shen *et al*, 1998; Khan *et al*, 2002; Silvio *et al*, 2004; Guan and Zhang, 2004). With a growing interest in the use of essential oils in both the pharmaceutical and the food industries, a systematic examination of plant extracts for these properties has become increasingly important (El-Massry *et al*, 2002).

Nanling national nature reserve, the biggest ecosystem in Guangdong province, possesses abundant plant resource. However, no studies have been carried out on the aromatic plants in this reserve concerning either the chemical composition or the biological activities of their volatile oils. In this study, we analyzed the essential oils of five Magnoliaceae species

from the reserve forest. The structures of the compounds in the volatile fractions of these five species were elucidated satisfactorily for the first time by using GC-MS analysis as well as by comparison of their RI values with literature data. In addition, we also evaluated their antioxidant activities by using the  $\beta$ -carotene bleaching (BCB) test method.

## 1 Materials and Methods

### 1.1 Materials and reagents

Leaves from *Manglietia moto* Dandy, *Manglietia yunnanensis* Law, *Michelia chapensis* Dandy, *Michelia foveolata* Merr. ex Dandy and *Michelia maudiae* Dunn were collected in the forest of Nanling national nature reserve, Ruyuan county, by the help of Dadingshan mountain administration in July 2004. The plants were identified by comparison with the samples in the administration's botanical sample room.

Linoleic acid (Alfa Aesar, Germany) and  $\beta$ -carotene (Sigma-Aldrich, USA) were purchased from Beijing Super Chem. Com Inc. (Beijing, China). Butylated hydroxytoluene (BHT) and *n*-alkanes ( $C_8$ – $C_{20}$ , GC grade) were purchased from China drug group (Shanghai, China). Other chemicals were of HPLC or reagent grade.

### 1.2 Isolation of the essential oil

Fresh leaves were crushed into serum with water and essential oils were extracted from 180 g of leaves by hydrodistillation in a modified Clevenger apparatus for 3 h. The obtained oils were dried over anhydrous sodium sulphate and kept refrigerated until used. The percentage content of the oils was calculated on the basis of the fresh weight of plant material. The samples of the obtained essential oils were dissolved in *n*-hexane for GC-MS analyses. The physical characteristics of essential oils from the five magnoliaceae species are listed in Table 1.

### 1.3 Analysis of the essential oils

Table 1 Physical characteristics of the essential oils from five Magnoliaceae species

	<i>M. moto</i>	<i>M. yunnanensis</i>	<i>M. chapensis</i>	<i>M. foveolata</i>	<i>M. maudiae</i>
Oil yield (%)	0.20	0.16	0.55	0.56	0.87
Color	Pale yellow	Bright yellow	Brown	Yellow	Colorless
Density (g/mL)	0.9366	0.9047	0.9930	0.9493	0.8666

Chemical constituents of the volatile oils were separated on a Finnigan TRACE/DSQ GC/MS instrument (Thermo Finnigan, USA), equipped with a DB-5 (30 m  $\times$  0.25 mm; 0.25  $\mu$ m film thickness) fused silica capillary column. Initial oven temperature was maintained at 40  $^{\circ}$ C for 1 min and then programmed at

10  $^{\circ}$ C/min to 200  $^{\circ}$ C (held 3 min); injector temperature, 220  $^{\circ}$ C; ion source temperature, 200  $^{\circ}$ C; EI, 70 eV; carrier gas, He at 1 mL/min; injection type, splitless (1  $\mu$ L of a 1:1000 hexane solution); mass range, 50–350 *m/z*. The constituents were identified by computer search (NIST Library 2002).

and by comparing their retention indices (RI) with literature values measured on columns with identical (Adams, 2001). An  $n$ -alkane hydrocarbon mixture ( $C_8$ – $C_{20}$  series) was injected under the above temperature program to calculate the RI using the following equation:

$$RI = 100n + 100(t_x - t_n)/(t_{n+1} - t_n)$$

where  $t_x$ ,  $t_n$  and  $t_{n+1}$  are the retention times of compound  $x$  and  $n$ -alkanes with the number of carbon atoms in the molecule  $n$  and  $n+1$ , respectively ( $t_n < t_x < t_{n+1}$ ) (Isidorov *et al.*, 2004). Relative concentrations (%) of identified compounds were calculated by integrating peak areas assuming a unity response by all.

#### 1.4 Determination of antioxidant activity with the $\beta$ -carotene bleaching (BCB) test

Antioxidant activities of the five Magnoliaceae species volatile oils were determined according to slightly modified version of the  $\beta$ -carotene bleaching method (Kulisic *et al.*, 2004). The  $\beta$ -carotene (0.1 mg) was added to a boiling flask together with linoleic acid (20 mg) and Tween 40 (100 mg), all dissolved in chloroform. After evaporating to dryness, under vacuum at 50°C by a rotary evaporator, oxygenated distilled water (50 ml) was added and the mixture was emulsified for 1 min in a sonicator to form emulsion A. 200  $\mu$ l of ethanolic stock solution of each antioxidant (concentration of stock solutions were 4, 8, 12, 16, and 20 g/L), was mixed with 5 ml of emulsion A in open-capped cuvettes. A control, without antioxidant, consisting of 200  $\mu$ l of ethanol and 5 ml of emulsion A was prepared. A second emulsion (B) consisting of 20 mg of linoleic acid, 100 mg of Tween 40 and 50 ml oxygenated water was also prepared. Ethanol (200  $\mu$ l), to which 5 ml of emulsion B was added, was used to zero the spectrophotometer. Readings of all samples were taken immediately ( $t = 0$  min) and at 15 min intervals for 120 min on a UV-visible spectrophotometer (916, GBC, Australia) at 470 nm. The cuvettes were therostated at 50°C between measurements. All determinations were performed in triplicate. The percentage inhibition was calculated from the data with the slightly modified formula (Mallet *et al.*, 1994):

$$\% \text{inhibition} = [(A_{A(120)} - A_{C(120)}) / (A_{C(0)} - A_{C(120)})] \times 100$$

where  $A_{A(120)}$  is the absorbance of the antioxidant at  $t = 120$  min,  $A_{C(120)}$  is the absorbance of the control at  $t = 120$  min, and  $A_{C(0)}$  is the absorbance of the control at  $t = 0$  min.

## 2 Results and Discussion

### 2.1 Chemical composition of the five essential oils

The oil yields obtained from the different species varied considerably (Table 1). The high oil yields

were obtained from *M. maudiae*, *M. foveolata* and *M. chapensis*. The oils of *M. foveolata* and *M. chapensis* species are deep incolor, while the *M. maudiae* oil shows no color.

Fifty seven to sixty six components could be identified, representing 97–98% of the oils, which are listed in Table 2 in order of their elution on a DB-5 column. The oils of two *Manglietia* species, *M. moto* and *M. yuyanensis*, were both constituted mainly by sesquiterpenoids (83.93% and 93.99%, respectively) and showed a high consistence of composition and some similarities in major constituents (also shown in Fig. 1). The *M. moto* and *M. yuyanensis* oils were dominated together with  $\delta$ -cadinol (20.57 and 6.92%), (*E*)-nerolidol (14.61 and 11.92%),  $\delta$ -cadinene (6.42 and

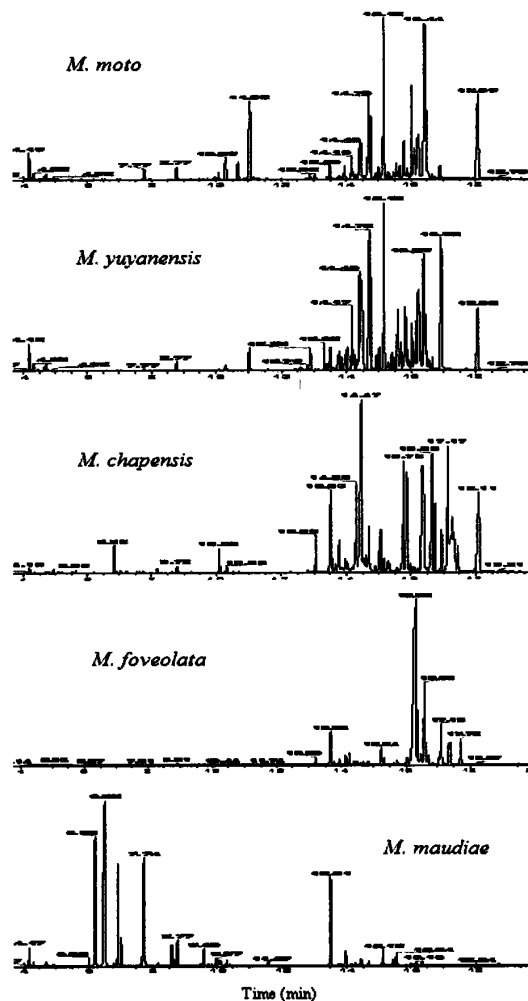


Fig. 1 Total ion current chromatogram of the essential oils of five Magnoliaceae species

Table 2 Volatile constituents ( % ) identified in the essential oils from five Magnoliaceae species

Constituents	RI <sup>lit. a</sup>	Magnoliaceae species					Identified methods
		<i>M. moto</i> (RI) <sup>b</sup>	<i>M. yunnanensis</i> (RI)	<i>M. chapensis</i> (RI)	<i>M. foveolata</i> (RI)	<i>M. maudiae</i> (RI)	
3-hexen-1-ol	859	0.12 (856)	0.11 (856)	0.13 (856)	0.10 (862)	0.17 (855)	GC-MS & RI
tricyclene	927	Tr <sup>c</sup> (920)	Tr (920)	Tr (921)	/	0.60 (921)	GC-MS & RI
α-thujene	930	Tr (927)	Tr (927)	Tr (927)	Tr (931)	16.00 (929)	GC-MS & RI
camphene	954	Tr (948)	Tr (947)	/	Tr (953)	26.08 (949)	GC-MS & RI
sabinene	975	Tr (968)	/	0.87 (969)	/	0.26 (969)	GC-MS & RI
β-pinene	979	Tr (971)	Tr (973)	Tr (972)	Tr (974)	10.54 (974)	GC-MS & RI
myrcene	991	0.05 (982)	Tr (982)	0.06 (982)	Tr (985)	2.04 (982)	GC-MS & RI
α-terpinene	1017	Tr (1013)	Tr (1013)	Tr (1014)	/	0.10 (1013)	GC-MS & RI
p-cymene	1025	Tr (1021)	Tr (1021)	Tr (1022)	/	0.16 (1021)	GC-MS & RI
d-limonene	1029	Tr (1025)	Tr (1025)	0.06 (1025)	Tr (1036)	12.54 (1027)	GC-MS & RI
1, 8-cineole	1031	0.55 (1031)	0.07 (1031)	/	/	/	GC-MS & RI
γ-terpinene	1060	Tr (1058)	Tr (1058)	0.13 (1060)	/	0.23 (1058)	GC-MS & RI
terpinolene	1089	Tr (1087)	Tr (1087)	Tr (1087)	/	1.67 (1087)	GC-MS & RI
α-p-dimethyl styrene	/	Tr (1093)	Tr (1094)	/	/	0.60 (1093)	GC-MS
linalool	1097	0.71 (1102)	0.36 (1102)	0.26 (1102)	0.27 (1108)	2.21 (1102)	GC-MS & RI
allo-ocimene	1132	/	/	/	/	0.13 (1129)	GC-MS & RI
trans-pinocarveol	1139	Tr (1142)	Tr (1143)	Tr (1143)	/	0.19 (1143)	GC-MS & RI
camphor	1146	Tr (1148)	Tr (1150)	Tr (1151)	Tr (1153)	1.62 (1150)	GC-MS & RI
bicyclo [ 2.2.1 ] heptan-2-ol, 2, 3, 3-trimethyl	/	Tr (1158)	Tr (1158)	Tr (1159)	Tr (1158)	0.22 (1158)	GC-MS
borneol	1169	0.26 (1173)	Tr (1173)	Tr (1174)	/	0.69 (1173)	GC-MS & RI
p-menth-1-en-4-ol	1177	0.55 (1180)	0.06 (1180)	1.25 (1181)	0.06 (1183)	1.02 (1180)	GC-MS & RI
p-menth-1-en-8-ol	1196	1.62 (1192)	0.28 (1192)	0.31 (1194)	0.10 (1193)	0.74 (1192)	GC-MS & RI
trans-carveol	1216	1.32 (1216)	0.05 (1216)	Tr (1218)	Tr (1218)	0.09 (1218)	GC-MS & RI
geraniol	1253	6.76 (1246)	1.14 (1246)	Tr (1246)	Tr (1256)	Tr (1256)	GC-MS & RI
p-menth-3-en-2-one	1258	0.10 (1256)	/	Tr (1250)	/	/	GC-MS & RI
bornyl acetate	1289	0.10 (1287)	0.10 (1287)	/	0.11 (1299)	0.32 (1287)	GC-MS & RI
δ-elemene	1338	0.08 (1338)	0.05 (1341)	0.07 (1339)	/	0.21 (1338)	GC-MS & RI
α-copaene	1377	0.10 (1377)	0.24 (1377)	0.10 (1378)	Tr (1380)	Tr (1377)	GC-MS & RI
β-cubebene	1388	0.27 (1388)	1.05 (1388)	Tr (1389)	/	0.06 (1388)	GC-MS & RI
β-elemene	1391	0.30 (1395)	0.05 (1395)	1.50 (1397)	Tr (1396)	0.09 (1395)	GC-MS & RI
α-cedrene	1412	Tr (1408)	/	/	0.78 (1408)	Tr (1408)	GC-MS & RI
β-caryophyllene	1419	Tr (1419)	1.16 (1418)	Tr (1416)	Tr (1418)	0.05 (1418)	GC-MS & RI
eremophil-1, 11-diene	/	0.14 (1424)	0.31 (1424)	Tr (1425)	0.16 (1427)	/	GC-MS
β-caryophyllene epoxy-	1425	6.79 (1425)	1.04 (1426)	4.06 (1427)	3.78 (1445)	10.01 (1427)	GC-MS & RI
α-trans-bergamotene	1435	/	0.10 (1434)	/	/	0.14 (1436)	GC-MS & RI
isocaryophyllene	1438	0.05 (1442)	/	0.26 (1444)	/	/	GC-MS & RI
α-humulene	1455	0.30 (1452)	1.53 (1453)	2.02 (1454)	0.20 (1450)	0.16 (1450)	GC-MS & RI
alloaromadendrene	1460	0.10 (1458)	0.68 (1458)	0.20 (1456)	Tr (1454)	0.11 (1458)	GC-MS & RI
9-epi-(E)-caryophyllene	1466	0.76 (1467)	0.71 (1467)	0.44 (1468)	0.52 (1465)	1.18 (1467)	GC-MS & RI
epi-bicyclosesquiphellandrene	1469	/	0.95 (1472)	0.31 (1473)	Tr (1472)	/	GC-MS & RI
gemacrene D	1485	1.76 (1483)	3.41 (1483)	Tr (1484)	1.11 (1480)	0.20 (1483)	GC-MS & RI
δ-selinene	1493	0.21 (1493)	0.11 (1493)	4.52 (1495)	1.05 (1489)	0.27 (1493)	GC-MS & RI
β-bisabolene	1506	1.56 (1501)	4.34 (1499)	/	0.36 (1502)	/	GC-MS & RI
gemacrene A	1509	3.41 (1507)	6.92 (1507)	16.05 (1507)	0.30 (1508)	0.77 (1506)	GC-MS & RI
(Z)-γ-bisabolene	1515	/	/	0.47 (1515)	0.21 (1514)	/	GC-MS & RI
δ-cadinene	1523	6.42 (1523)	10.84 (1524)	2.12 (1522)	0.28 (1522)	0.40 (1522)	GC-MS & RI
cadin-1, 3, 5-triene	/	3.60 (1528)	4.10 (1529)	/	/	/	GC-MS
isolongifol-8-ol	/	Tr (1532)	Tr (1532)	Tr (1531)	0.27 (1531)	/	GC-MS
trans-cadin-1 (2), 4-diene	1535	/	/	0.25 (1534)	0.28 (1534)	Tr (1534)	GC-MS & RI
α-cadinene	1539	0.33 (1540)	0.84 (1540)	/	Tr (1540)	/	GC-MS & RI
α-calacorene	1546	0.49 (1545)	1.03 (1545)	0.62 (1545)	/	Tr (1544)	GC-MS & RI
hedycaryol	1550	/	/	1.49 (1549)	0.11 (1548)	Tr (1548)	GC-MS & RI
(E)-nerolidol	1563	14.61 (1558)	11.92 (1558)	0.41 (1557)	Tr (1557)	1.15 (1555)	GC-MS & RI
β-calacorene	1566	/	/	0.44 (1565)	2.00 (1563)	0.09 (1561)	GC-MS & RI
3-hexen-1-ol benzoate	1567	0.60 (1568)	0.68 (1568)	0.37 (1569)	0.72 (1568)	/	GC-MS & RI
ledol	1569	0.05 (1576)	0.61 (1576)	Tr (1576)	Tr (1577)	/	GC-MS & RI

Continued table 2

Constituents	RI <sup>lit. a</sup>	Magnoliaceae species					Identified methods
		<i>M. moto</i> (RI) <sup>b</sup>	<i>M. yunnanensis</i> (RI)	<i>M. chapensis</i> (RI)	<i>M. foveolata</i> (RI)	<i>M. maudiae</i> (RI)	
caryophyllenyl alcohol	1572	0.41 (1580)	0.43 (1580)	/	/	0.59 (1579)	GC-MS & RI
globulol	1585	1.11 (1586)	3.42 (1589)	0.19 (1585)	0.12 (1584)	1.14 (1585)	GC-MS & RI
geraniol	1601	0.89 (1594)	1.25 (1594)	/	0.25 (1594)	0.10 (1597)	GC-MS & RI
epi-cubenol	1619	/	/	/	0.41 (1599)	/	GC-MS & RI
C15H20O (M= 204)	/	/	Tr (1604)	6.63 (1604)	/	/	GC-MS
C15H20O (M= 216)	/	2.1715.81	2.7115.83	4.7715.86	Tr15.87	0.1015.87	GC-MS
10-epi- $\gamma$ -eudesmol	1624	0.99 (1616)	1.19 (1616)	0.16 (1618)	/	Tr (1617)	GC-MS & RI
C15H24 (M= 204)	/	5.51 (1630)	3.37 (1630)	0.10 (1630)	1.04 (1629)	0.17 (1629)	GC-MS
$\gamma$ -eudesmol	1632	1.81 (1636)	2.55 (1640)	0.16 (1636)	Tr (1640)	0.58 (1642)	GC-MS & RI
$\alpha$ -muurolol	1646	5.31 (1649)	7.70 (1649)	0.13 (1647)	/	/	GC-MS & RI
$\alpha$ -eudesmol	1654	/	/	/	49.70 (1657)	/	GC-MS & RI
C15H24O (M= 220)	/	/	/	10.08 (1663)	2.50 (1664)	0.45 (1663)	GC-MS
$\delta$ -cadinol	1674	20.57 (1669)	6.92 (1665)	/	0.81 (1674)	/	GC-MS & RI
eudesma-4(15), 7-dien-1 $\beta$ -ol	1688	0.20 (1684)	0.32 (1684)	/	13.74 (1685)	0.10 (1680)	GC-MS & RI
$\alpha$ -bisabolol	1686	0.23 (1692)	0.66 (1692)	7.85 (1692)	/	/	GC-MS & RI
C15H20O (M= 216)	/	/	/	2.53 (1700)	1.03 (1697)	0.05 (1697)	GC-MS
vaticenene	/	/	/	/	0.12 (1707)	/	GC-MS
(Z, Z)-farnesol	1718	0.75 (1712)	7.78 (1714)	1.55 (1714)	/	Tr (1712)	GC-MS & RI
(E, E)-farnesol	1725	0.10 (1730)	0.06 (1730)	10.02 (1729)	7.43 (1727)	Tr (1727)	GC-MS & RI
C10H14O (M= 150)	/	/	/	8.46 (1739)	/	/	GC-MS
limonene-6-ol, pivalate	/	0.05 (1744)	Tr (1744)	/	4.45 (1744)	/	GC-MS
aromadendrene oxide-(2)	/	0.06 (1751)	Tr (1752)	0.96 (1751)	/	/	GC-MS
farnesene epoxide, E-	/	/	/	/	3.21 (1770)	/	GC-MS
C15H22O (M= 218)	/	8.44 (1797)	3.96 (1795)	6.06 (1797)	0.06 (1791)	0.21 (1793)	GC-MS
C13H18O (M= 190)	/	/	/	/	0.34 (1837)	/	GC-MS
trans-Z-bisabolene epoxide	/	/	/	/	0.18 (1856)	/	GC-MS
nerolidyl acetate	/	/	/	/	0.16 (1891)	/	GC-MS
phytol	1943	0.35 (1931)	0.20 (1931)	/	/	0.34 (1931)	GC-MS & RI
monoterpene hydrocarbons		0.05	Tr	1.12	Tr	70.95	
oxygenated monoterpenes		12.03	2.07	10.28	4.99	7.10	
sesquiterpene hydrocarbons		27.54	46.25	33.72	13.12	15.14	
oxygenated sesquiterpenes		56.39	47.74	52.56	79.50	3.33	
Others		1.07	1.04	0.50	1.16	0.51	
Total		97.08	97.10	98.31	98.32	97.03	

<sup>a</sup> RI<sup>lit.</sup> = Retention indices published by Adams (DB-5 column).      <sup>b</sup> RI= Retention index relative to C<sub>8</sub>-C<sub>20</sub> n-alkanes on DB-5 column.

<sup>c</sup> Tr= trace compounds (concentration less than 0.05%).

10.84%),  $\alpha$ -muurolol (5.31 and 7.70%), germacrene A (3.41 and 6.92%) and an unknown oxygenated sesquiterpene (8.44 and 3.96%), respectively. Of course, there were content differences in some constituents, such as  $\beta$ -caryophyllene (6.79 and 1.04%), geraniol (6.76 and 1.14%), and (Z, Z)-farnesol (0.75 and 7.78%), respectively, between them. The high consistence of composition and similarities in major constituents may indicate their close correlation between relatives. However, the three oils of *Michelia* species are quite different. The oils of *M. chapensis* and *M. foveolata* were constituted mainly by sesquiterpenoids (86.28% and 92.62%,

respectively), while the oil of *M. maudiae* was dominated with monoterpenes (78.05%), and there was no similarity in major constituents between them. The principal constituents of the *M. chapensis* oil were germacrene A (16.05%), (E, E)-farnesol (10.02%),  $\alpha$ -bisabolol (7.85%), three unknown oxygenated sesquiterpenes (10.08, 6.63, and 6.06%, respectively) and an unknown oxygenated monoterpene (8.46%). The *M. foveolata* oil showed distinguishable composition and its principle constituents were  $\alpha$ -eudesmol (49.70%), eudesma-4(15), 7-dien-1 $\beta$ -ol (13.74%) and (E, E)-farnesol (7.43%). Whereas, the *M. maudiae* oil was mostly dominated with monoterpene hydrocar-

bons such as camphene (26.08%),  $\alpha$ -thujene (16.00%), D-limonene (12.54%) and  $\beta$ -pinene (10.54%), with the exception of  $\beta$ -caryophyllene (10.01%).

## 2.2 Antioxidant activities of the five essential oils

The BCB method is based on the loss of the yellow color of  $\beta$ -carotene due to its reaction with radicals which are formed by linoleic acid oxidation in an emulsion. The rate of  $\beta$ -carotene bleaching can be slowed down in the presence of antioxidants (Kulisic *et al.*, 2004). This principle is also used in the antioxidant activity evaluation of the essential oils of five magnoliaceae species in comparison with BHT and ascorbic acid.

As a result of  $\beta$ -carotene bleaching caused by the oxidation of linoleic acid, the absorbance of the test solutions decreased with time (Fig. 2). The discoloration process in the model system progressed differently for the various samples. The control sample without addition of antioxidant oxidized decreased most rapidly, and the *M. maudiae* sample also showed this trend. The rate of  $\beta$ -carotene bleaching in the *M. moto* sample was most effectively slowed down suggesting its most potent antioxidant power among the five essential oils.

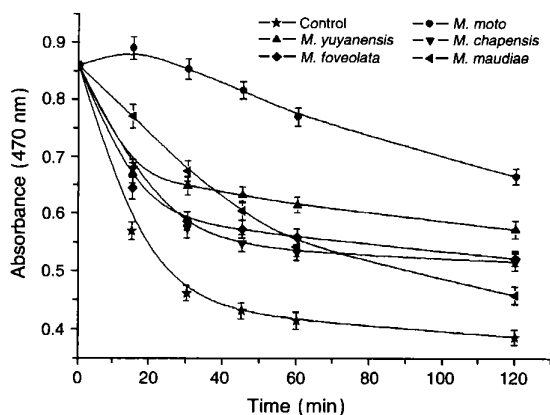


Fig. 2 Rate of  $\beta$ -carotene bleaching in control without antioxidant and the essential oils of five magnoliaceae species.

The concentration of the total oils was 8 g/L

Fig. 3 shows the antioxidant activities of the five essential oils in the comparison with those of BHT and ascorbic acid. The antioxidant power decreased in the order BHT > essential oils > ascorbic acid. BHT was the strongest antioxidants. In comparison, the essen-

tial oils except *M. maudiae* oil showed relatively significant antioxidant activity, while ascorbic acid showed no antioxidant effect. Among the five oils, the *M. moto* and *M. maudiae* samples expressed the strongest and faintest antioxidant efficacy in this evaluation method, respectively. The concentration remarkably influenced the antioxidant power of each oil sample except ascorbic acid. The 50% inhibition were accomplished with less than 2.0 g/L of BHT, 6.6 g/L of *M. moto* oil, 9.8 g/L of *M. yuyanensis* oil, 11.3 g/L of *M. foveolata* oil, and 12.2 g/L of *M. chapensis* oil, respectively, whereas ascorbic acid and *M. maudiae* oil could not inhibit 50% of the bleaching reaction under the test conditions.

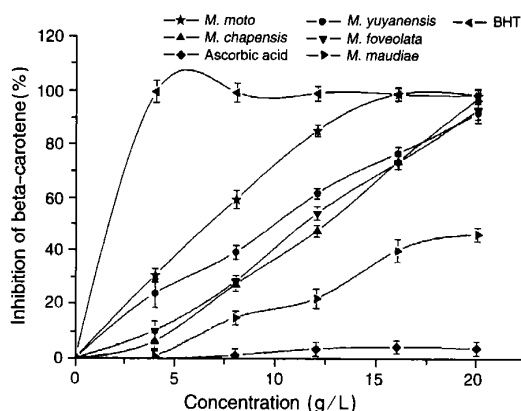


Fig. 3 Antioxidant activity of the essential oils of five magnoliaceae species, BHT and ascorbic acid with  $\beta$ -carotene bleaching method

It is interesting to note that the difference of antioxidant effect between the *M. maudiae* oil and other four oils was remarkable. This can be explained, to some extent, by comparing the reported antioxidant efficacy of some individual aromatic components with the principle constituents and their proportions in these oils. Ruberto and Baratta (2000) evaluated the antioxidant efficacy of almost 100 pure components of essential oils with lipid system. The results showed that the antioxidant efficacy of essential oil was mainly contributed by the class of oxygenated monoterpene and oxygenated sesquiterpene components (generally, phenols > allylic alcohols > aldehydes). Moreover, a scarce antioxidant activity is normally accredited to monoterpene hydrocar-

bons except terpinolene,  $\alpha$ -terpinene,  $\gamma$ -terpinene and sabinene (Kamal-Eldin *et al.*, 1996). However, the *M. maudiae* oil characterizes high contents of camphene,  $\alpha$ -thujene, and  $\beta$ -pinene (Table 2), which possess of low antioxidant activity. Because of the BCB method employs an emulsified lipid system, it could not show the antioxidant properties of ascorbic acid (a well known polar antioxidant). This phenomenon was formulated as the “polar paradox” which has been reported earlier (Frankel *et al.*, 1994; Koleva *et al.*, 2002). The polar antioxidants remaining in the aqueous phase of the emulsion are more diluted in lipid phase and are thus less effective in protecting the linoleic acid.

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